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Extremely strong OH···O hydrogen bonds in some 3-organophosphorus substituted pentane-2,4-diones

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Abstract

Single crystal X-ray analysis showed that 2-(2′,4′-dioxo-3′-pentyl)-*trans*,*trans*-4,6-dimethyl-2-oxo-1,3,2-dioxaphosphorinane (**I**) exists in the enol form, exhibiting hydrogen bonding with an R(O···O) of 2.397 Å.

X-ray and NMR data (δ, $\Delta\delta$(H–D)) for 3-organophosphorus substituted pentane-2,4-diones revealed strengthening of the hydrogen bonding by the introduction of phosphorus substituents into pentane-2,4-dione, as a result of steric effects. The content of the enol form has also been determined.

INTRODUCTION

Enol tautomers of 1,3-diketones display the shortest hydrogen bonds in neutral molecules [1]. Substitution at C(2) results in strengthening of the OH···O bond, which is evident from the shortening of the R(O···O) distance to less than 2.45 Å [2–5]. The shortest hydrogen bond for 1,3-diketones has been observed in cyclic usnic acid [6], due to delocalization.

In our view, all the substituents at C(3) of pentane-2,4-dione can be divided into three groups, according to their influence on the structure of the enol form and the tautomerism.

(1) Alkyl substituents such as Me and Et, which are neither bulky nor electron-withdrawing, belong to the first type. In this case strong hydrogen bonding and high enolization are observed.

(2) In the case of non-bulky, electron-withdrawing substituents (aryl,

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